

PROGRESS IN COAL PYROLYSIS RESEARCH

Peter R. Solomon and Michael A. Serio
Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108

KEYWORDS: Pyrolysis, Coal, Crosslinking

INTRODUCTION

This paper considers some of the recent progress in both the improved understanding and the identification of areas uncertainty with regard to coal pyrolysis, rates, and mechanisms. The paper addressed two questions:

- what are the controlling chemical factors in coal pyrolysis?
- what are the controlling physical factors in coal pyrolysis?

The factors considered are summarized in Table 1. The problem of answering the questions is that multiple chemical reactions occur whose results depend on how the reactants are bound in the coal macromolecular network. Species-selective transport of the reactants and products further complicate the interpretations. In what follows, we have tried to focus on topics where answers are needed or where significant new progress is being made.

TABLE 1

FACTORS WHICH CONTROL COAL PYROLYSIS

<u>CHEMICAL</u>	<u>PHYSICAL</u>
Bond Breaking Reactions	Tar Vaporization
Retrogressive / Crosslinking Reactions	Viscosity
Effects of Cations	Network Effects
Effects of H ₂ O	
Effects of O ₂	
Network Effects	

Chemical Factors

Bond Breaking - The bond breaking reactions can be separated into two broad categories, those which release small molecular side groups attached to the macromolecular network and those which break bonds holding the network together to form a collection of fragments called *metaplast*. Study of the former category is easier because, in this case, reactions of a limited number of identifiable functional groups lead (without significant mass transfer limitations) to the production of a limited number of identifiable gas species. The chemistry has been organized into global reactions of functional groups to form specific products.

Study of the latter category of reactions is particularly complicated because: i) the reactants are large, heterogeneous and often insoluble; ii) multiple reactions are generally required to free a product, and iii) removal of products from the reacting *metaplast* is subject to mass transfer limitations. Global rates can be determined for the overall reactions.

In general, all reaction rates need to be represented by a distribution of reaction parameters about an average (e.g., a Gaussian distribution of activation energies) because of the heterogeneous chemical nature of coals. While much progress has been made in describing the classes of reactions and measuring global rates, a quantitative description of the detailed chemistry of pyrolysis is not yet possible. This objective remains as an important goal.

Of particular interest is the systematic rank dependence of the reaction rates (the rates for all reactions decrease with increasing rank) which has recently been reported (1-3). These experiments were performed at several low heating rates where the temperature of coal particles can be accurately determined and hence the rates accurately measured. Experiments at high heating rates, in which coal particle temperatures are measured (4-9), indicate that extrapolation of the rates measured at low heating rates to high heating rates is reasonable. In addition, some progress has been made in considering higher rank coals to be the results of nature's pyrolysis of lower rank coals in the coal bed over millions of years. These analyses employ pyrolysis rates extrapolated to the lower bed temperatures (6,10,11). For some pyrolysis products, nature's removal of the higher reaction rate part of the distribution can explain the systematic shift in the average rate with rank. This is illustrated in Figure 1 which compares the water evolution curves during pyrolysis of several Argonne coals with predictions for Zap lignite after a simulated maturation at various temperatures.

Crosslinking - Crosslinking reactions are particularly hard to identify because the products are insoluble. Crude measurements can be made of "crosslink density" without identification of the specific crosslinking bond. Such measurements are made by solvent swelling (12) or carbon NMR (9,13). In addition, measurements of the mobile phase by proton NMR (14,15) or by solvent extraction (16) provide data on the variation in the concentration of mobile molecules as they are formed or linked into the network.

The results from pyrolysis studies at heating rates between 0.5 and 1000 K/sec show that crosslinking is rank dependent, with lignites crosslinking at lower temperatures than bituminous coals (17,18). Crosslinking in lignites occurs prior to tar evolution and the rapid loss of weight and aliphatic hydrogen. Crosslinking in high volatile bituminous coals occurs at temperatures slightly higher than the temperature for maximum tar evolution, weight loss, and aliphatic hydrogen loss.

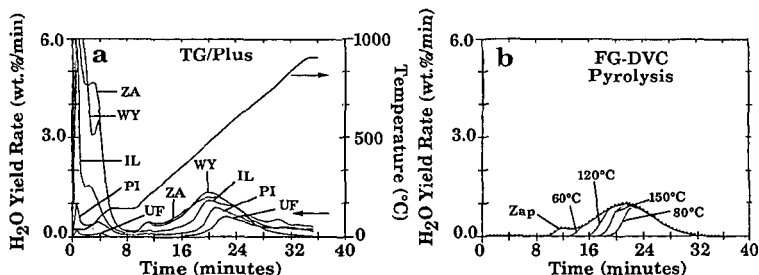


Figure 1. Evolution of H₂O from Five Argonne Premium Coals: (a) Pyrolyzed at 30 K min⁻¹; (b) Predicted for Slow Pyrolysis (geological ageing) at Different Temperatures followed by Pyrolysis at 30 K min⁻¹. ZA, Beulah Zap Lignite; WY, Wyodak Anderson Subbituminous; IL, Illinois No. 6 HVB; PI, Pittsburgh No. 8 HVB; UF, Upper Freeport MVB. (from Ref. 6).

Studies correlating the crosslink density with other pyrolysis reactions have identified a connection between low temperature crosslinking and CO₂ (and possibly H₂O evolution). These low temperature crosslinking reactions are also related to a loss of carbonyl and hydroxyl functional groups in the coal (17), which is consistent with a loss of carboxyl groups. Similarly, a correlation exists between moderate temperature crosslinking and CH₄ evolution, and high temperature condensation of the macromolecular network and H₂ evolution (17,18).

As in the case of bond breaking reactions, global pathways and rates have been identified for crosslinking reactions but the detailed chemistry is still an important target for study.

Effects of Cations - Crosslinking has also been observed to be influenced by the presence of alkali metals, whose removal increases pyrolysis tar yields (19-22). These results would indicate that the role of carboxyl groups, as indicated above, is important, but it is the carboxylate (cation exchanged carboxyls) which are the key agents in retrogressive reactions for low rank coals. The role of calcium in reducing liquefaction yields from low rank coals has been suggested in previous work by Mochida et al. (23) and Joseph and Forrai (24). It is also consistent with work which shows an effect of calcium on reducing pyrolysis tar yields (19-22). The role of calcium may be to provide a nascent crosslink site in the coal by allowing coordination of groups like carboxyl and hydroxyl which are prone to such reactions. Otherwise, these sites would be more likely to coordinate with water (through hydrogen bonding) than with each other.

Effects of H₂O - The presence of water appears to have a profound effect on the course of pyrolysis. Effects of water during pyrolysis have been studied by Lewen (25) and Monthieux and Landais (26). The impact of water is illustrated in Figure 2 modified from Ref. 26.

The figure presents the atomic H/C ratio as a function of O/C ratio for several pyrolysis experiments. For the line labeled path 1, the pyrolysis system is open and pyrolysis products escape the pyrolysis vessel as they are formed. For these experiments, both oxygen and hydrogen are lost in comparable amounts as pyrolysis proceeds. For path 2, the pyrolysis system is closed. Pyrolysis products fill the pyrolysis vessel and can re-react with the pyrolyzing char. The result is a reduction in the loss of hydrogen and an increase in the loss of oxygen. For path 3, the system is confined to minimize any space into which pyrolysis products can escape. Under these conditions, the loss of hydrogen is further retarded, while the loss of oxygen is accelerated. The path taken by the char is now similar to nature's maturation sequence shown by the shaded band in Fig. 2 for coals from the same bed. The interpretation of these results, as well as the other hydrous pyrolysis experiments suggests that the presence of water due to the confinement of the system results in significant changes in the pyrolysis chemistry. Since the loss of oxygen functional groups is desirable to improve liquid yields from

pyrolysis and liquefaction, and since it is one of the dominant mechanisms in the maturation of coal, understanding and controlling these reactions involving H_2O is an important target.

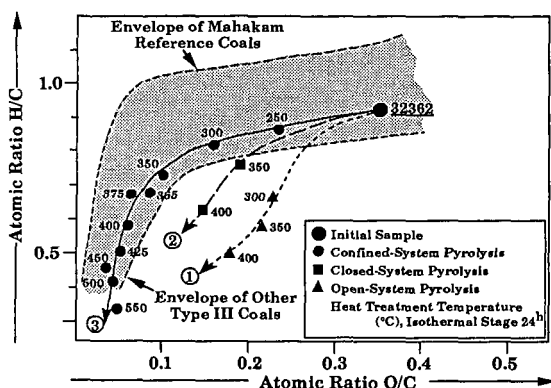


Figure 2. Influence of Confinement Conditions on Elemental Composition of Pyrolysis Chars (from Ref. 26).

Oxygen - The effect of oxygen on coal pyrolysis is most often exhibited through weathering. Low temperature oxidation of the coal results in reduced yields of tar and liquids as well as reduced fluidity. A feature of coal oxidation is that often a very small amount of oxygen added to the coal can cause significant effects in subsequent pyrolysis and liquefaction. Why oxidation has such a profound effect may be a result of changes in the network geometry as discussed in the next section.

Network Effects - Recognizing the macromolecular network nature of coal, a number of network models have been developed (27-30). These models assume the network to be made of thermally stable aromatic ring clusters connected by less stable bridges. When the network is heated, random cleavage of the less stable bridges leads to a collection of network fragments called the metaplast. The molecular weight distribution has been computed using chain statistics (31,32), percolation theory (6,29,30), and Monte Carlo methods (6,27,28). The lightest fraction of the metaplast can vaporize to form tar. Somewhat heavier molecules can be extracted. The heaviest molecules, which are mobile but are not easily extracted, and the extractable molecules provide the coal's fluidity. What is important about the network models is the effect of the network geometry (i.e., whether it is a chain-like or fish-net-like) on the products of pyrolysis. This effect is illustrated in Fig. 3 (from Ref. 6) which presents the molecular weight distribution of network fragments as a function of the average number of bridges per cluster, α , for two geometries represented by the coordination number, $1 + \sigma$. The coordination number is the maximum number of bridge attachments per cluster. The figure presents results for $\sigma + 1 = 2.2$ (Fig. 3a) which is chain-like (1 extra bridge or crosslink every

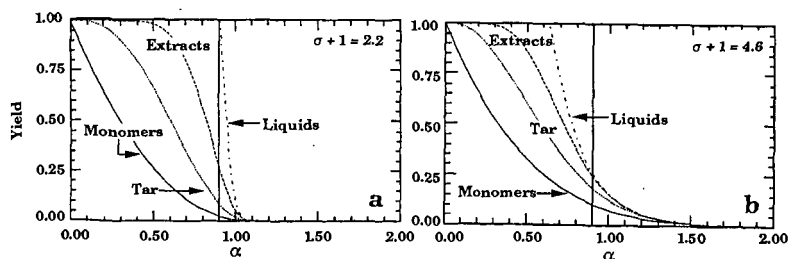


Figure 3. Percolation Theory Predictions for Macromolecular Network Fragment Molecular Weight Distribution as a Function of the Average Number of Attachments per Ring Cluster, α . For a) $\sigma + 1 = 2.2$; b) $\sigma + 1 = 4.6$ (from Ref. 6). Monomers are all Single Clusters. Tar Consists of Monomers, Dimers, and Trimers. Extracts Consist of Molecules up to 10-nmers and Liquids Consist of Molecules up to 100-nmers.

5th cluster) and $\sigma + 1 = 4.6$ (Fig. 3b) which is fish-net-like. As can be seen, the molecular weight distributions are quite different. In Fig. 3a there is nearly an even distribution of all molecular sizes, while in Fig. 3b the small molecules are favored. The former case would represent the highly fluid char of high volatile bituminous coal, while the latter would represent a non-softening (thermosetting) lignite or subbituminous coal. The importance of low temperature crosslinking events in low-rank coals or in oxidized high rank coals is that the network coordination number is increased. A few added crosslinks does not have a strong influence on the bond breaking chemistry, but rather changes the product distribution through its influence on the network geometry.

Physical Factors:

Tar Vaporization - The tar fraction in pyrolysis consists of molecules heavy enough to condense at room temperature. The source for this material is the small unattached "molecular" fraction of the network plus small molecular fragments produced by pyrolysis. The removal of these molecules is controlled by mass transfer including: vaporization, diffusion, and convective transport. The removal process is in competition with the repolymerization process. Recent models suggest that the tars reach their equilibrium vapor pressure (or close to it) in the light gases produced in pyrolysis and are transported through the char primarily by convection through the pores or by bubble motion (6,28,33,34).

Fluidity - The fluidity of coal as it is heated is typically measured with a Geissler plastometer. High to medium volatile bituminous coals exhibit the highest fluidities. As temperature increases, measurable fluidity appears at a temperature of 350°C. The initial fluidity is reversible and is attributed to physical melting (35). As temperature increases, fluidity increases due to irreversible bridge breaking reactions and then decreases due to crosslinking (36). Low temperature crosslinking in low rank coals can prevent the onset of any observable fluidity.

Models relate fluidity to the amount of the liquid or mobile phase (16,36-38) which can be predicted from network models (6,27-30,35). Experiments which measure the liquid content or mobile phase (14-16) all show similar temperatures for the onset, peak and disappearance of the coal fluidity (6).

Network Effects - The physical effects (tar formation, solvent interactions, and fluidity) are related to the molecular weight distribution of small molecules in the coal, the network fragments forming the metaplast during pyrolysis, and the bonding forces holding these molecules together. Thus, the effect of the network is important because of the effect of network geometry on the molecular weight distribution (see Fig. 3). Low temperature crosslinking in low rank coals leads to a high effective coordination number and hence low amounts of tar and extracts and low fluidity. The lack of such crosslinking in bituminous coals leads to high yields of extracts and tars and high fluidity. Thus, the application of macromolecular network models appears to unify many observations of coal pyrolysis including tar formation, extract formation, metaplast formation, fluidity, and solvent swelling behavior.

CONCLUSION

The progress during the past ten years of research in coal science has resulted in the maturation of many new experimental techniques to follow coal conversion chemistry including NMR, XPS, XANES, FT-IR, ESR, TG-FTIR, solvent swelling, solvent extraction, and MS. These techniques have been used on coals, chars, tars, extracts, model compounds, and model polymers containing natural and isotopically labeled compounds to follow the chemistry in a variety of coal conversion experiments. The results have led to a new understanding of bridge breaking and crosslinking and their variations induced by solvents, catalysts, water, and oxygen. The results have also led to new macromolecular network models of coal pyrolysis and liquefaction. Such models provide a vastly improved global understanding of coal conversion behavior, but detailed understanding of the controlling reactions has not yet been achieved. Such detailed understanding and the resulting strategies for controlling the conversion behavior is the central challenge of coal science in the future.

ACKNOWLEDGEMENTS

Much of the work performed by the authors was supported by the Morgantown Energy Technology Center of the Department of Energy under Contract No. DE-AC21-86MC23075.

REFERENCES

1. Burnham, A.K., Oh, M.S., Crawford, R.W., and Samoun, A.M., *Energy & Fuels*, **3**, 42, (1989).
2. Solomon, P.R., Serio, M.A., Carangelo, R.M., Bassilakis, R., Gravel, D., Baillargeon, M., Baudais, F., and Vail, G., *Energy & Fuels*, **4**, (3), 319, (1990).
3. Serio, M.A., Solomon, P.R., Charpenay, S., Yu, Z.Z., and Bassilakis, R., *ACS Div of Fuel Chem. Preprints*, **35**, (3), 808, (1990).

4. Solomon, P.R., Serio, M.A., and Markham, J.R., Kinetics of Coal Pyrolysis, Int. Conference on Coal Science Proceedings, IEA, Tokyo, Japan, p. 575, (October 23-27, 1989).
5. Serio, M.A., Hamblen, D.G., Markham, J.R., Solomon, P.R., *Energy and Fuel*, **1**, 138, (1987).
6. Solomon, P.R., Hamblen, D.G., Serio, M.A., Yu, Z.Z., and Charpenay, S., *Fuel*, **72**, 649, (1993).
7. Fletcher, T.H., *Combust. Sci. and Tech.*, **63**, 89, (1989).
8. Fletcher, T.H., "Time-Resolved Particle Temperature Measurements and Mass Loss Measurements of a Bituminous Coal during Devolatilization", *Combustion and Flame*, **78**, 223, (1989).
9. Fletcher, T.H., Solum, M.S., Grant, D.M., and Pugmire, R.J., *Energy and Fuels*, **6**, 643, (1992).
10. Braun, R.L., Burnham, A.K., and Reynolds, J.G., *Energy and Fuel*, **6**, 468, (1992).
11. Solomon, P.R., Serio, M.A., Carangelo, R.M., Bassilakis, R., Yu, Z.Z., Charpenay, S., and Whelan, J., *J. Anal. and Appl. Pyrol.*, **19**, 1-14, (1991).
12. Green, T.K., Kovac, J., and Larsen, J.W., *Fuel*, **63**, 935, (1984).
13. Solomon, P.R., Charpenay, S., Yu, Z.Z., Serio, M.A., Kroo, E., Solum, M.S., and Pugmire, R.J., "Changes During Coal Pyrolysis: Experiment and Theory", presented at the 1991 Int. Conf. on Coal Science, New Castle, England, (Sept. 1991).
14. Marzec, A., Jurkiewicz, A., and Pislewski, N., *Fuel*, **62**, 996, (1983).
15. Lynch, L.J., Webster, D.S., Sakurovs, R., Barton, W.A., and Maher, T.P., *Fuel*, **67**, 579, (1988).
16. Fong, W.S., Peters, W.A., and Howard, J.B., *Fuel*, **65**, 251, (1986).
17. Solomon, P.R., Serio, M.A., Deshpande, G.V., and Kroo, E., *Energy and Fuels*, **4**, 42, (1990).
18. Suuberg, E.M., Lee, D., and Larsen, J.W., *Fuel*, **64**, 1668, (1985).
19. Tyler, R.J. and Schafer, H.N.S., *Fuel*, **59**, 487, (1980).
20. Morgan, M.E. and Jenkins, *Fuel*, **65**, 764, (1986).
21. Serio, M.A., Kroo, E., Teng, H., Solomon, P.R., *ACS Div. of Fuel Chem. Preprints*, **38** (2), 577 (1993).
22. Wornat, M.J. and Nelson, P.F., *Energy and Fuel*, **6** (2), (1992).
23. Mochida, I., et al., *Fuel*, **62**, 659, (1983).
24. Joseph, J.T. and Forrai, T.R., *Fuel*, **71**, 75 (1992).
25. Lewen, M.D., in *Organic Geochemistry*, (M.H. Engel and S.A. Macko, Eds.), Plenum Press, NY, Chapter 24, to be published.
26. Monthieux, M. and Landais, P., *Energy and Fuels*, **2**, 794, (1988).
27. Gavalas, G.R., *Coal Pyrolysis*, Elsevier, NY, p. 51 (1982).
28. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A., and Deshpande, G.V., *Energy and Fuel*, **2**, 405, (1988).
29. Grant, D.M., Pugmire, R.J., Fletcher, T.H., and Kerstein, A.R., *Energy and Fuels*, **3**, 175, (1989).
30. Niksa, S. and Kerstein, A.R., *Fuel*, **66**, 1389, (1987).
31. Solomon, P.R. and King, H.H., *Fuel*, **63**, 1302, (1984).
32. Niksa, S., and Kerstein, A.R., *Combustion and Flame*, **66**, 95, (1986); see also *Energy and Fuels*, **5**, 647, (1991).
33. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. and Deshpande, G.V., *Combustion and Flame*, **71**, 137, (1988).
34. Niksa, S., *AIChE J.*, **34**, (5), 790, (1988).
35. Waters, P.L., *Fuel*, **41**, 3, (1962).
36. Solomon, P.R., Best, P.E., Yu, Z.Z., and Charpenay, S., *Energy & Fuel*, **6**, 143, (1992).
37. Fong, W.S., Khalil, Y.F., Peters, W.A., and Howard, J.B. *Fuel*, **65**, 195, (1986).
38. Oh, M.S., "Softening Coal Pyrolysis", Ph.D. Thesis, Massachusetts Institute of Technology, (1985).